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Solar fuels and inspiration from photosynthesis

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ABSTRACT

The generation of renewable electricity is becoming increasingly cost-effective and efficient so that a different set of challenges have arisen that need to be overcome. The most pressing of these is the development of viable, 'green' ways to store this energy as carbon–carbon bonds. Natural photosynthesis provides a ready blue print for the conversion of solar energy into carbohydrate, *i.e.*, a fuel composed of carbon–carbon bonds. Natural photosynthesis is too complicated and its components too fragile ever to be copied in an artificial context. Natural photosynthesis, however, does provide many templates that can be mimicked in any future bio-inspired version of artificial photosynthesis, such as the oxygen evolving complex and the enzyme RuBisCO. Many options will need to be explored to find the best ways to achieve artificial photosynthesis and to achieve it will require a large-scale, coordinated international effort. There is simply no time left to continue in the way we are now. Climate change needs to be stopped as soon as possible and the clock is ticking for us to make clean, renewable solar fuels. We must all now work together!

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1. The context

Climate change is a global problem that requires a co-ordinated, ambitious and large scale research program to halt or, indeed, to reverse it. The evidence, accumulated over the past few years, is now overwhelming and clearly shows that this problem has been caused by mankind's unrestrained consumption of fossil fuels. The realisation of this central point is the reason so many countries came together last year (2016) in Paris, under the auspices of the United Nations, to develop an ambitious plan to combat climate change. It is, however, often difficult to persuade countries that they should allow their own research funding to be spent on transnational research projects where they would also be paying for research carried out by foreign scientists working outside the funding country's borders. This requires the funding countries to put aside narrow self-interest and to have the confidence that these funded projects are the optimal ones to solve the problem, in this case to mitigate climate change. To overcome the very practical issues involved, a 'Grand Challenge' approach has been proposed in an open letter that was published in Nature [1]. This type of approach has been previously used to great effect in tackling major health related diseases (http://www.grandchallenges.org/). In this approach, a panel of the world's best experts come together to establish a road map that sets out research steps needed to overcome the problem, with the best international teams then assembled to carry out the required science. This process allows both governments and philanthropic funders to be fully assured that their money is being appropriately spent. More recently in Marrakesh a group of twenty-three countries and the EU agreed to establish Mission Innovation. The aim of this forum is to coordinate increased funding to tackle both climate change and the problems it is causing. Table 1 details the seven major areas that were identified where this effort should be focused. In the context of this paper it is Challenge No. 5, 'Converting Sunlight Innovation Challenge – to discover affordable ways to convert sunlight into storable solar fuels,' that is relevant here. Research into artificial photosynthesis, the subject of our recent conference, is designed exactly to do this. Currently electricity can be efficiently produced from clean renewable sources of energy using solar panels, wind turbines, etc. [2–4]. However, we do not yet have sufficiently 'smart' grids to properly cope with the complicated problems associated with mid- to long-term electricity generation, such as; the transition from fossil fuels to renewables, the intermittency of renewable sources of energy and the difficulty in storing large amounts of electricity for long periods of time [5]. It is apparent

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Table 1
The seven Innovation Challenges identified by Mission Innovation.

1. Smart Grids Innovation Challenge – to enable future grids that are powered by affordable, reliable, decentralised renewable electricity systems
2. Off-Grid Access to Electricity Innovation Challenge – to develop systems that enable off-grid households and communities to access affordable and reliable renewable electricity
3. Carbon Capture Innovation Challenge – to enable near-zero CO_2 emissions from power plants and carbon intensive industries
4. Sustainable Biofuels Innovation Challenge – to develop ways to produce, at scale, widely affordable, advanced biofuels for transportation and industrial applications
5. Converting Sunlight Innovation Challenge – to discover affordable ways to convert sunlight into storable solar fuels
6. Clean Energy Materials Innovation Challenge – to accelerate the exploration, discovery, and use of new high-performance, low-cost clean energy materials
7. Affordable Heating and Cooling of Buildings Innovation Challenge – to make low-carbon heating and cooling affordable for everyone

The Innovation Challenges are each advanced by a voluntary coalition of participating MI members, under the co-leadership of two to four countries.

ways of storing electricity in chemical bonds are urgently needed, *i.e.*, as a fuel, and artificial photosynthesis aims to do exactly this.

2. Lessons from the natural to the artificial forms of photosynthesis

It has become popular to label almost all research on harvesting solar energy to make fuel as artificial photosynthesis, irrespective as to whether these studies are bioinspired or not. It is worthwhile, therefore, to take a step back and consider what biology teaches us about photosynthesis. In other words, what are the key features about making solar fuels that should be learned from the natural process?

Photosynthesis begins with the absorption of a photon by a light-harvesting system. There are a large variety of different types of light-harvesting complexes found in Nature [6,7] and some of these are illustrated in Fig. 1. It is, certainly, difficult at first glance to see any general principles in these structures but they are there. Different light-harvesting complexes have evolved to allow efficient absorption of the wavelengths of the solar spectrum that are available to photosynthetic species in any particular ecological niche. For example, higher plants are, in general, exposed to the full solar spectrum available at the surface of the earth and have chlorophyll as the main light-harvesting pigment (Fig. 1C). In contrast, dinoflagellates that live in the water column in oceans at depths where only blue light is available have carotenoid as their major light-harvesting pigments (Fig. 1B). The structures of the

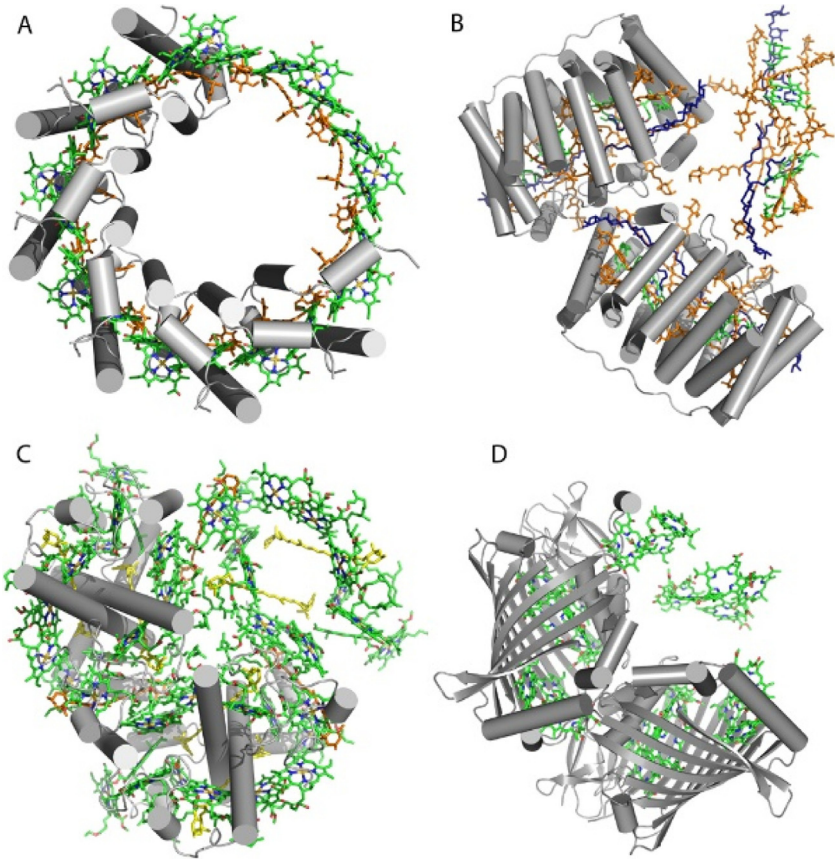

Fig 1. An illustration of some of the structural diversity within different types of biological light harvesting complexes found in Nature. The tertiary structure protein scaffolds are given in grey cylinders for α-helices or flat strands for β-sheet as appropriate. For each case one of the protein monomers has been removed to facilitate a clearer view of the constituent pigment arrangement. (A) The light-harvesting II complex (LH2) from the purple, non-sulphur bacterium *Rhodospeudomonas acidophila* 10050 (PDB 1KZU). Bacteriochlorophyll *a* – green, rhodopin glucoside (carotenoid) – orange. (B) The peridinin-chlorophyll-protein (PCP) from the dinoflagellate *Amphidinium carterae* (PDB 1PPR). Chlorophyll *a* – green, peridinin (carotenoid) – orange. (C) The major light-harvesting complex II (LHCII) from spinach (PDB 1RWT). Chlorophylls – green, lutein (carotenoid) –yellow, xanthophyll (caroteinoid) – orange (D) The Fenna-Matthews-Olson Protein from the green, sulphur bacterium *Chlorobaculum tepidum* (PDB 3ENI). Bacteriochlorophyll *a* – green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

different types of light-harvesting pigment protein complexes reflect the necessary structural requirements to package the different types of pigments. In most cases the pigments are non-covalently bound to their apoproteins. These polypeptides exquisitely position the pigments with respect to the distances between them and the relative orientation of the transitions dipole moments of the pigments' excited states that are involved in the energy transfer reactions. The apoproteins also control the spectroscopic and photochemical properties of the light-harvesting pigments. For example, in the purple bacterial light-harvesting complexes the Q_y transition bands in the bound bacteriochlorophyll *a* molecules absorb anywhere between 800 and 980 nm, depending on the apoproteins involved (Fig. 1A) [8]. It is now clear that the natural process of biological light-harvesting has evolved

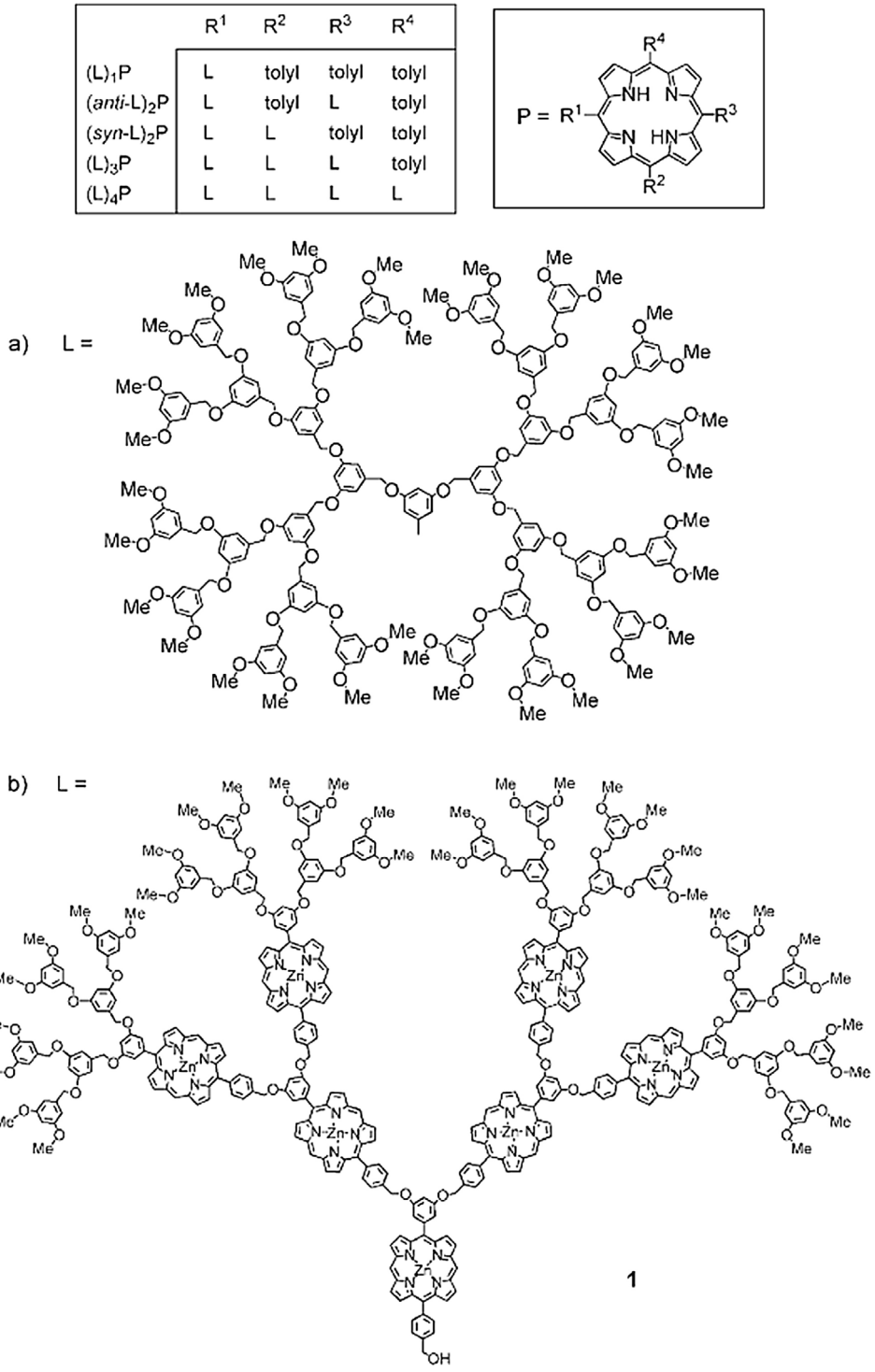
R1 R2 R3 R4
(L)1P L tolyl tolyl tolyl
(anti-L)2P L tolyl L tolyl
(syn-L)2P L L tolyl tolyl
(L)3P L L L tolyl
(L)4P L L L L
P = R1 R4 R3 R2 NH N N HN
a) L =
b) L =
1

Fig. 2. The chromophore porphyrin is used extensively in natural photosynthesis as the chromophore in chlorophyll and its derivatives. Therefore, this molecule was an obvious candidate for the construction of artificial antenna systems. Promising morphology-dependent light-harvesting studies have been performed for a series of dendrimers with the general formula (L)nP, where P is a free-base porphyrin core bearing different numbers (n = 1–4) of dendrons (L) at its meso positions and L is either (A) poly(benzyl ether) dendrons [9] or (B) much larger dendrons each containing seven Zn-porphyrin units [10]. (A) is reprinted (adapted) with permission from [9]. Copyright 2017 American Chemical Society and (B) is reprinted (adapted) with permission from Wiley.

by engineering the protein matrix in which the light-harvesting pigments are embedded. Up until now most attempts at producing artificial light-harvesting assemblies have only involved synthesising covalently attached arrays of pigments, *e.g.*, Fig. 2 [9,10]. Nobody has attempted yet to place these pigments into a scaffold matrix equivalent to a protein, so that this matrix then influences the pigment's properties to constructively promote efficient light-harvesting. The role of a smart matrix in facilitating the chemical reactions in photosynthesis will be a recurring theme in this short feature article. It has been known for a long time that dense solutions of pigments, such as chlorophylls, show a phenomenon known as concentration quenching [11,12]. A casual look at the different types of photosynthetic light-harvesting complexes may give the impression that the arrangement of the pigments is random. This prompts the question as to how concentration quenching is prevented in these systems. The answer is that the positioning of the chlorophylls, for example, is not actually random, rather they are precisely positioned to prevent concentration quenching. If the position of the chlorophylls in the core complex of photosystem I are compared in cyanobacteria [13] with those in higher plants [14], it is evident that they are essentially the same (see Fig. 3). This similarity is due to the functional constraints placed upon the complex. There are so few ways, in which to position densely-packed chlorophylls so that they don't exhibit concentration quenching yet also allow efficient light-harvesting. In addition to light-harvesting, photosynthetic complexes typically have an important built-in photo-protective capability. When the amount of light impinging upon a light-harvesting complex becomes too high the resultant chlorophyll excited singlet states can persist long enough to allow intersystem crossing to produce excited triplet states. These triplet states typically last from microseconds to milliseconds and is long enough to react with molecular oxygen generating singlet oxygen [15]. Singlet oxygen is a very powerful and destructive oxidizing agent that can destroy most large bio-molecules. By including carotenoids in their major chlorophyll containing light-harvesting complexes they are protected from such harmful reactions [16]. Carotenoids extend the spectral wavelengths harvested by the complex but they also rapidly quench chlorophyll triplet states before they can react with oxygen [17]. This reaction then generates carotenoid triplet states that are too low in energy to sensitize the formation of singlet oxygen and so the excess energy decays harmlessly as heat (see Fig. 4). So far very little attempt has been made to synthesize artificial light-harvesting pigment arrays that are photo-protected.

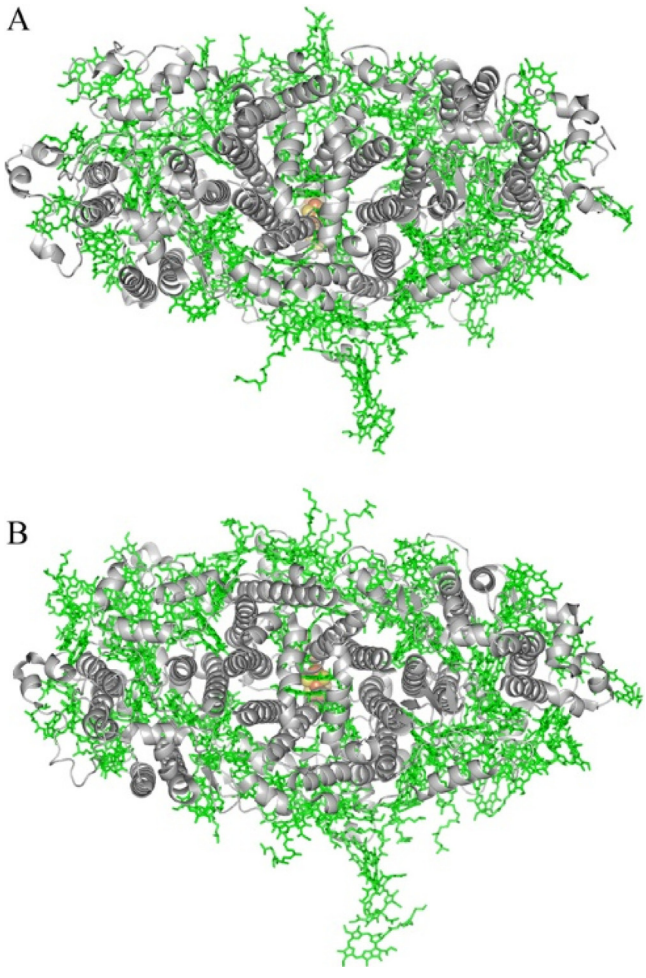

Fig. 3. After millions of years of evolution, the arrangement of the chlorophylls (green) in the core complex of photosystem I is very similar in both (A) the cyanobacteria *Synechococcus elongatus* (PDB 1JB0) and (B) in pea (PDB 5L8R). The positioning of the chlorophylls is not random, rather they are precisely positioned by the protein (grey) to prevent concentration quenching. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Light energy absorbed by the light-harvesting apparatus is transferred rapidly and efficiently to specialized pigment protein complexes called reaction centers [18]. In the reaction centers the excitation energy is used to drive a series of redox reactions that result in charge separation across the photosynthetic membrane and the absorbed solar energy is 'trapped' and converted into useful chemical energy [19–21]. There are two types of reaction centers in photosynthesis that clearly have evolved from a single common ancestral reaction center. These are the Type 1 and Type 2 reaction centers [21,22]. The overall structures of both types of reaction center are very homologous with the redox active pigments arranged into two arms bound non-covalently by two integral membrane proteins that each have 5 transmembrane spanning alpha helices. The arrangement of the redox cofactors in these two types of reaction center is depicted in Fig. 5. The chain of cofactors is one of the design principles that ensures that the charge separation reactions have a high quantum yield [18]. Each forward electron transfer step slows the back reaction by about three orders of magnitude so that the final charge separated state is stabilized long enough for the subsequent electron transfer reactions to occur and to prevent energy-wasteful back reactions. Type 1 reaction centers produce a strong reductant that is then used to reduce NADP to NADPH [13,14]. Type 2 reaction centers produce a strong oxidant that is accumulated in stages to allow the stepwise oxidation of water [23]. The two reaction centers, therefore, co-operate to catalyze the flow of electrons from water to NADP. During the electron flow between the two reaction centers, energy is conserved in the form of a transmembrane proton motive force and used to drive the synthesis of ATP by the well-known chemiosmotic mechanism [21,24]. Photosystem II is the site of water oxidation and photosystem I is the site of NADP reduction. When water is split by photosystem II, the waste product produced is oxygen and, unlike the electrolysis of water when molecular hydrogen is produced, hydrogen ions (protons) and electrons are released. It is worth spending a bit more time considering the way in which water splitting is accomplished by photosystem II. Unfortunately, all photosystem II X-ray crystal structures suffer from some degree of radiation-induced Mn reduction, however, the so-called oxygen evolving complex (OEC) on the oxidizing side of photosystem II has now been studied by and visualized at relatively high resolution by X-ray crystallography [25], femtosecond X-ray free electron lasers [26,27], EXAFS [28], advanced EPR techniques [29] and theoretical calculations [30]. The OEC structure is shown in Fig. 6. At its center are four manganese ions that act as a charge accumulator [31,32]. They

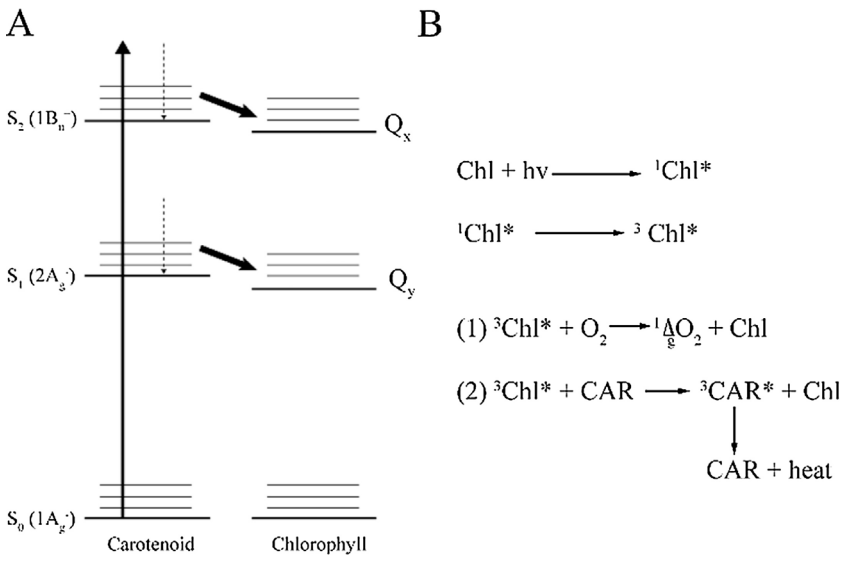

Fig. 4. (A) A simplified diagram for energy transfer between the two, low-lying singlet excited states of carotenoids and (bacterio)chlorophyll molecules. The one-photon allowed S_2 ($1B_u^+$ state) is responsible for the strong optical absorption in the blue-green spectral region, whereas the S_1 ($2A_g^-$ state) is one-photon forbidden. The lifetimes of these singlet excited states and the S_1 and S_2 energy levels depend on the extent of conjugation (n): when $n > 13$ these levels are below the Q_x and Q_y levels and the carotenoid cannot act as a photo-harvester. Although recent findings of other low-lying one-photon forbidden, excited singlet states of carotenoids have made the story more complicated, in general, the efficiency of carotenoid-to-Bchl energy transfer depends on how effectively the energy can be harvested from both these excited states. (B) (Bacterio)chlorophylls when irradiated undergo intersystem crossing to produce excited triplet states. These triplets are sufficiently long-lived and energetic enough to interact with ground state oxygen to produce singlet oxygen. Carotenoids do not directly quench this reaction by interacting with singlet oxygen (1), rather their low-lying triplet state quenches the chlorophyll triplet state before they can interact with molecular oxygen (2). It is difficult to directly measure the energy level of the carotenoid triplet but empirical evidence from photosynthetic complexes suggests that only carotenoids with $n > 7$ are able to perform this reaction.

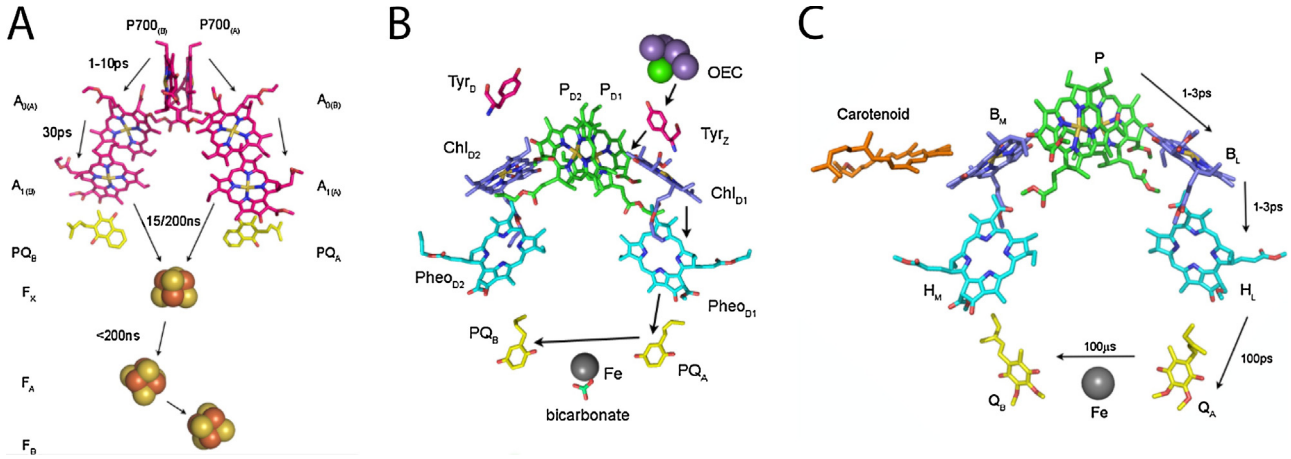

Fig. 5. A comparison between Type I and Type II reaction centers. (A) Photosystem I (PDB 1JB0) is a Type I reaction center with the incoming light energy to P_{700} being used to excite an electron that is able to pass down both branches of pigments (Chls P_{700}, A0, A1 (magenta) and phylloquinones (yellow)) to the iron-sulphur complexes (F_X, F_A, and F_B) and then to reduce the mobile carrier ferredoxin. (B) Photosystem II (PDB 3BZ1) is a Type II reaction center with the incoming light energy to P_{680} being used to excite an electron that is able to pass down both only one side of pigments (Chls P_{680} (green), Chl D_1 (mauve), pheophytin D_1 (cyan) and plastoquinones PQ_A and PQ_B (yellow)). Electrons are supplied to P_{680} from the water-splitting reactions mediated in the OEC (Fig. 6). (C) The purple bacterial reaction center is also Type II and so is organisationally very similar to photosystem II. There is no OEC in purple photosynthetic bacteria and so light-energy is used to directly excite an electron that passes down only one branch (Chls P_{860} (green), accessory Bchl (mauve), bacteriopheophytin (cyan) and ubiquinones Q_A and Q_B (yellow)) to reduce the mobile carrier, Q_B. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

store four positive charges and then oxidize two molecules of water in a concerted reaction that then releases one molecule of oxygen. During the charge accumulation reactions one charge is produced every time photosystem II turns over and 'pulls' an electron from the manganese cluster. In order to prevent a local Coulomb expulsion, protons are moved to provide charge compensation [30]. This is another example where the matrix (i.e., the protein), in which the redox cluster is embedded, actively participates in the catalytic mechanism. As with the case of light-harvesting pigment mimics mentioned previously, no currently synthesized oxygen evolving mimics have their redox cluster housed in a responsive (smart) matrix. It is not sufficient to just mimic the structure of the manganese cluster and expect it to be a good catalyst. The message from biology is that the matrix matters!

The light reactions in photosynthesis can then be compared with a photocell that is used to charge up a battery. The primary light driven reactions in photosynthesis involve driving a charge separation reaction. The subsequent electron transfer and chemical reactions (these will be described below) then ultimately

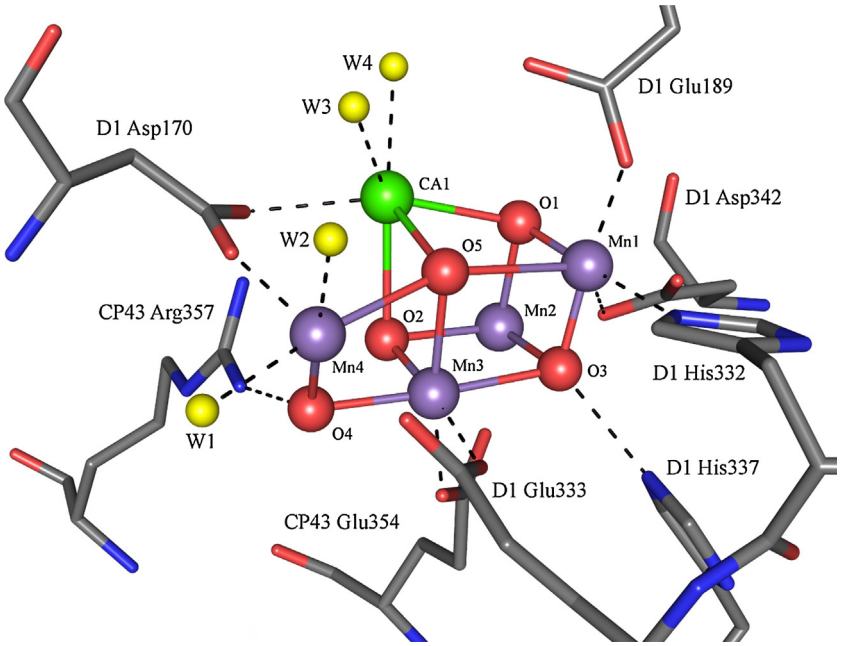

Fig. 6. The OEC is the enzyme responsible for photosynthetic water oxidation and is comprised of a Mn_4CaO_5 cluster embedded in the photosystem II protein matrix (PDB 3WU2). The oxygen atoms form μ-oxo bridges linking the metal atoms as a hetero-cubane motif with a dangler Mn (Mn4) connected to the cubane via an additional μ-oxo bridge. Ca^{2+} and Mn4 each have two terminal water ligands (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

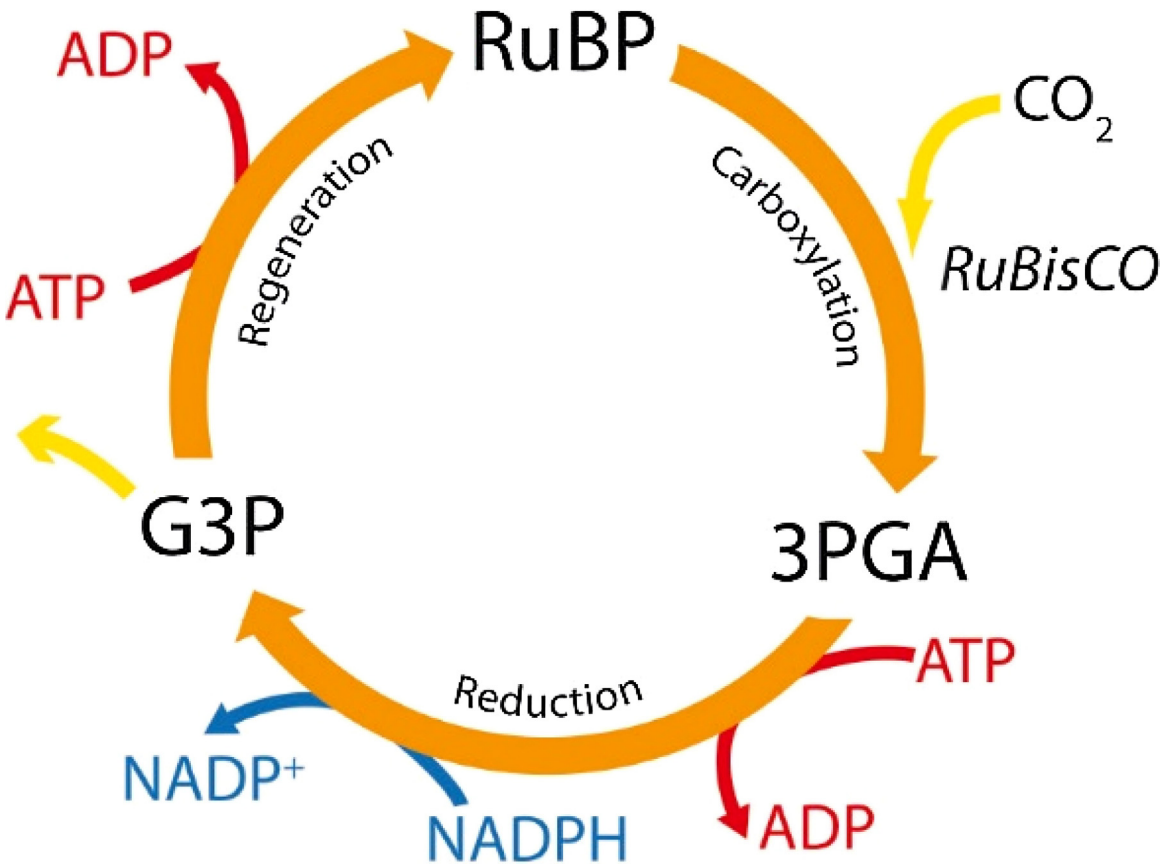

Fig. 7. The Calvin-Benson cycle is a complex series of reactions that uses the high-energy, high-potential molecules to produce the precursor molecule glyceraldehyde 3-phosphate (G3P) that is converted into glucose and other carbohydrates. The five-carbon molecule ribulose 1,5-bisphosphate (RuBP) is carboxylated through the action of RuBisCO and two molecules of the three carbon 3-phosphoglycerate (3PGA) are formed. 3PGA is phosphorylated and reduced using ATP and NADPH to G3P. For every six molecules of G3P formed, one leaves as a precursor to glucose and the remaining five are regenerated to form three molecules of RuBP by using more ATP and the cycle can begin again.

reduce atmospheric carbon dioxide to produce glucose (*i.e.*, the fuel). If in an artificial photosynthetic system light is harvested by a photocell to produce voltage, then somehow coupling the direct use of electrons to chemistry to produce fuel is the challenge that needs to be overcome. It should be realized that biology adopts a different strategy. The light reactions in photosynthesis produce reduced NADP and ATP [33]. These two chemicals provide the chemical potential and, therefore, the driving force required to allow ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) to fix atmospheric carbon dioxide and the Calvin cycle enzymes to fully reduce it to glucose [33]. Using a photocell at the front end of an artificial photosynthesis system is attractive since the overall efficiency of the photocell can be higher than that of photosynthesis and the solar cell is much more robust than pigment-protein complexes involved in the early reactions of photosynthesis [34]. The major outstanding challenge is how to couple the photocell to catalysts that can reduce atmospheric carbon dioxide to a fuel under normal atmospheric conditions *i.e.*, at 0.04% CO_2.

Photosynthesis uses the Calvin-Benson cycle to fix CO_2 and to reduce it to carbohydrate [33], illustrated in Fig. 7. The key step in this cycle is the initial carboxylation reaction catalyzed by RuBisCO in C-3 plants to convert ribulose-1,5-bisphosphate (RuBP) into 3-phosphoglycerate (3PGA). This enzyme, probably the most abundant on Earth, first appeared when the atmospheric concentrations of CO_2 were much higher than they are today [35]. The carboxylase function of the enzyme started to face serious problems as the CO_2 present in the atmosphere was slowly replaced by oxygen as oxygenic photosynthesis became dominant. This is because the affinity of RuBisCO for CO_2 is rather low, yet this could be partially overcome by making more enzyme to compensate. Chloroplasts, therefore, today contain very high amounts of RuBisCO to ensure that even if the enzyme's affinity for CO_2 is low some activity can be retained. However, the prevalence of O_2 over CO_2 then led on to an even bigger problem. Due to the electrostatic similarity between the two gases, and the large imbalance in their atmospheric abundances, it is hard for RuBisCO to completely discriminate between them [36]. If O_2 out-competes CO_2 at the RuBisCO active site, then RuBP is oxidised resulting in the formation of 2-phosphoglycolate (2PGA) and the release of the pre-fixed CO_2 back into the atmosphere (Fig. 8), although some of the carbon is recovered using organelles called peroxisomes through a metabolically expensive pathway. Evolution has not been able to 'improve' RuBisCO to overcome photorespiration, although other partial solutions have evolved. Both C-4 [37] and Crassulacean acid metabolism (CAM) plants [38] have evolved to enable these types of plants to grow in arid, hot and dry environments, rather than as a specific mechanism to overcome photorespiration *per se*. However, cyanobacteria have evolved to contain intracellular protein-based structures called carboxysomes, in which RuBisCO is packaged very densely, as a clever mechanism to overcome respiration [39] (see Fig. 9). These structures have reduced oxygen permeability coupled with a transport system to concentrate CO_2 so that RuBisCO can function with less oxygen impairment. The problems with the activity of RuBisCO is one of the major reasons why the overall efficiency of photosynthesis is relatively low [40] and why RuBisCO is often thought of as a rather poor catalyst [41]. It is important, however, to realize that no man-made catalyst is able to activate CO_2 under ambient atmospheric conditions. Even with its problems RuBisCO is effective. Every single atom of carbon in our bodies was pulled out of the air by RuBisCO!

3. Going forward

Recently Dan Nocera has used his understanding of both chemistry and biology to build a novel system that can use solar energy to drive the synthesis of a carbon-based fuel [42]. His prototype system starts with the splitting of water by electrolysis, powered by a solar cell and facilitated by catalytic, cobalt/phosphate electrodes for the oxygen evolution, and NiMoZn

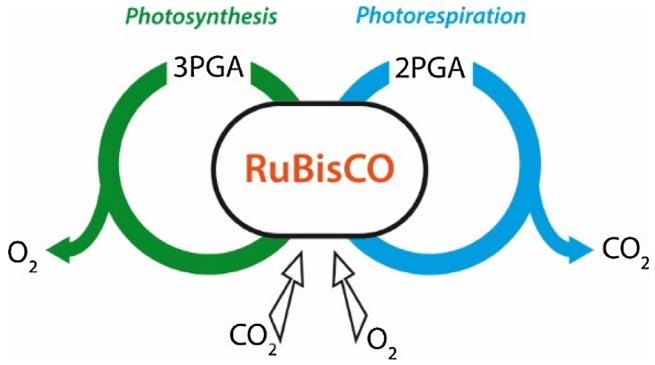

Fig. 8. RuBisCO does not discriminate well between CO_2 and O_2. If O_2 is the substrate then for every two molecules of the five-carbon RuBP, two molecules each of 3PA and 2-phosphoglycerate (2PGA) are formed with the loss of one CO_2 molecule. As one molecule of O_2 is consumed, one molecule of CO_2 is released the overall light-driven process is called photorespiration. Two 2PGA molecules are recycled through peroxisomes and mitochondrion, using a complicated metabolic pathway into one 3PGA at the cost of five ATP and three NADPH molecules.

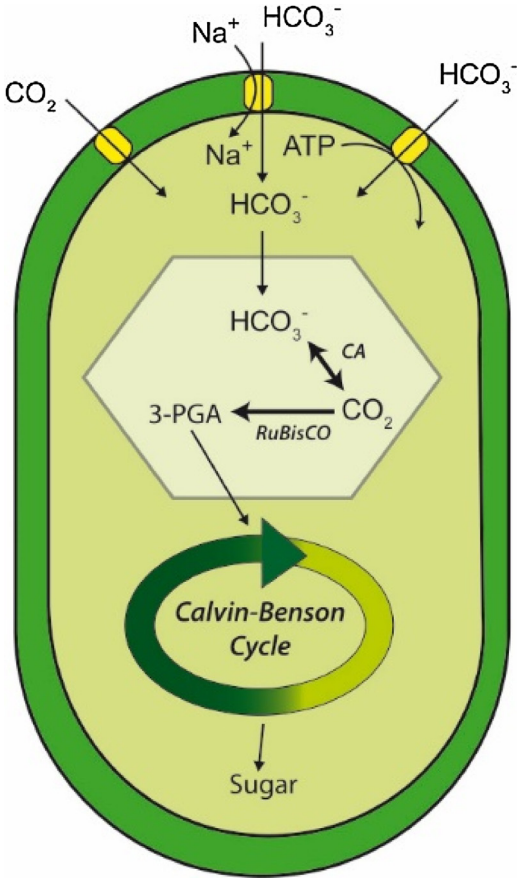

Fig. 9. Carboxysomes are polyhedral protein bounded organelles present in some photosynthetic organisms that are involved in concentrating CO_2 as a means of bypassing the wasteful oxygenase activity present RuBisCO. Carbon is transported into the cell in the form of bicarbonate ions rather than CO_2. Bicarbonate diffuses into the carboxysome and is rapidly converted to CO_2. This results in an increased local concentration of CO_2, and a correspondingly low concentration of O_2, resulting in efficient turnover of CO_2 into 3PGA by RuBusCO.

electrodes for hydrogen evolution. These electrodes reduce the over-potential required to drive the water splitting reactions and the cobalt/phosphate electrodes are self-healing. The hydrogen that is produced is then provided to the anaerobic bacterium *Ralstonia eutropha* where hydrogenases use it as a source of energy to drive the incorporation of CO_2 into polyhydroxybutyric acid (PHB), a carbon storage product [43]. The overall energy efficiency for the incorporation of CO_2 powered by the hydrogen is approximately 50%. This is an interesting system as it combines both the use of a solar cell to initially harvest solar energy with enhanced efficiency and the power of biology in the form of the enzymes to carry out the conversion of CO_2 into PHB. With the advent of synthetic biology the 'biological module' in this set up can be changed and/or optimized to provide not just PHB but a wide range of other products. This example is also useful to illustrate what can be achieved in this area when different scientific disciplines (chemistry, physics and synthetic biology) are brought together to tackle the problem. Unfortunately, it seems clear that a lot of research under the umbrella of 'artificial photosynthesis' is rather fragmented, with too many people just doing what they always have done but now badging it as artificial photosynthesis. Researchers in this area need to come together, decide on an integrated approach and begin to work together across many disciplines, in a much more coordinated way, if we are to achieve an efficient, functional and applied form of artificial photosynthesis in time. There are a few current initiatives where this is taking place; UNICAT in Berlin, the CIFAR program on Solar Fuels in Canada and the Swedish Artificial Photosynthesis Consortium in Uppsala are good examples. However, the clock is ticking towards irreversible global warming and that means time is of the essence.

Acknowledgements

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